

AD-A150 529

EFFECT OF SUBSTITUTED PHENYLNADIMIDES ON PROCESSING AND 1/1  
PROPERTIES OF PMR. (U) NATIONAL AERONAUTICS AND SPACE  
ADMINISTRATION CLEVELAND OH LE. W B ALSTON ET AL.

UNCLASSIFIED

1985 NASA-TM-86902 USARVSCOM-TR-84-C-20

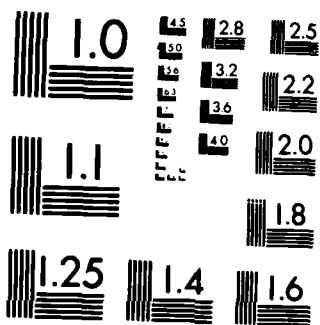
F/G 11/4

NL

END

FORMED

STIC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS 1963 A

(2)

# Effect of Substituted Phenylnadimides on Processing and Properties of PMR Polyimide Composites

AD-A150 529

William B. Alston  
Propulsion Laboratory  
AVSCOM Research and Technology Laboratories  
*Lewis Research Center*  
*Cleveland, Ohio*

and

Richard W. Lauver  
*Lewis Research Center*  
*Cleveland, Ohio*

SELECTED  
FEB 12 1985  
A D

DTIC FILE COPY

Prepared for the  
Thirtieth National SAMPE Symposium and Exhibition  
Anaheim, California, March 19-21, 1985

This document has been approved  
for public release and sale; its  
distribution is unlimited.



EFFECT OF SUBSTITUTED PHENYLNADIMIDES ON PROCESSING AND PROPERTIES OF  
PMR POLYIMIDE COMPOSITES

William B. Alston  
Propulsion Laboratory  
AVSCOM Research and Technology Laboratories  
Lewis Research Center  
Cleveland, Ohio 44135

and

Richard W. Lauver  
National Aeronautics and Space Administration  
Lewis Research Center  
Cleveland, Ohio 44135

SUMMARY

Three nitrophenylnadimide cure initiators and two phenylnadimides (without nitros) were evaluated as additives to PMR-15 resins and Celion 6000 graphite fiber composites. The results of a resin screening study eliminated all of the additives except 3-nitrophenylnadimide (NO<sub>2</sub>PN) for use as a low temperature curing additive for PMR-15. Thus, NO<sub>2</sub>PN and the two control additives were investigated in PMR-15 formulations from which Celion 6000 graphite fiber/PMR-15 composites were processed both with low temperature (274 °C) and normal (316 °C) cure cycles. Comparisons of the two processing cycles, the resultant glass transition temperatures (T<sub>g</sub>), the ambient, 274 and 316 °C composite mechanical properties determined before and after 316 °C postcure, the 316 °C thermo-oxidative weight losses and the retention of 316 °C composite mechanical properties are presented. Empirical correlations of the type and amount of nadimide additives with processing parameters, T<sub>g</sub>, composite mechanical properties, composite thermo-oxidative stability and long term retention of 316 °C composite mechanical properties are also presented. It was shown that PMR-15 composites could be fabricated using a low temperature (274 °C) cure with nitrophenylnadimide additives. However, the use of any type of phenylnadimide additives (nitro or non-nitro) or the lower temperature curing of PMR-15 without additives resulted in composites that exhibited a combination of decreased initial mechanical properties, lower retention of elevated temperature mechanical properties and/or increased composite weight loss compared to conventionally cured PMR-15 composites.

INTRODUCTION

The development of *in situ* Polymerization of Monomeric Reactants (PMR) Polyimides was first reported by investigators at the NASA Lewis Research Center (ref. 1). In subsequent studies (ref. 2) they reported that a methanol solution of 2.08 moles of the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE), 3.08 moles of 4,4'-methylenedianiline (MDA) and 2 moles of the monomethyl ester of endo-5-norbornene-2,3-dicarboxylic acid (NE) provided a highly processable matrix resin. This resin, designated PMR-15, when polymerized *in situ* on the fiber, provided an optimum balance of desirable composite processing characteristics, composite thermo-oxidative stability, and retention of composite mechanical properties after long term high temperature



A-1	
Distribution/	
Availability Codes	
Dist	Avail and/or Special

E-2380

aging. PMR represented a new technology of addition-cured polyimide matrix resins. Today, PMR-15 is commercially available from major suppliers of prepreg materials and is being used in a wide range of aerospace components (ref. 3).

PMR-15 has not gained even wider acceptance because the final cure temperature (316 °C) exceeds the temperature capabilities of many autoclaves. Several studies have been directed toward lowering the cure temperature of PMR-15. Two approaches to lowering the cure temperature are (1) the use of all meta-aminostyrene endcaps (ref. 4) and (2) the use of para-aminostyrene endcaps combined with NE endcaps (ref. 5). Both of these approaches provided about a 56 °C reduction in cure temperature. However, only the mixed endcap system provided 316 °C mechanical performance comparable to state-of-the-art PMR-15. The para-aminostyrene/NE system has more recently been modified (ref. 6) by the addition of small amounts of N-phenylnadimide (PN). This resin modification alleviated the need for higher processing pressures and provided composites having thermo-oxidative stability and composite 316 °C mechanical performance nearly equal to state-of-the-art PMR-15. A different approach to lower the cure temperature was investigated using resins containing carbomethoxy, phenyl or benzo substituted nadimides (ref. 7). Another approach to lower the cure temperature of PMR-15 has also been reported (ref. 8) which utilizes small amounts of nitrophenylnadimide additives and other nitro additives to PMR-15. These additives appear to increase the rate of nadimide polymerization at lower temperatures. The purpose of this report is to demonstrate the feasibility of using nitrophenylnadimides and other nitro substituted compounds to lower the cure temperature of PMR-15 composites and to identify the processing parameters and resultant composite performance characteristics.

## EXPERIMENTAL PROCEDURES

### Monomers and Additives

The monomers and additives used in this study are shown in Table I. The NE, MDA, DINO<sub>2</sub>TOL and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) were obtained as reagent grade chemicals from commercial sources and were used as received after verifying the melting points (mp). The PN, NO<sub>2</sub>PN, and DINO<sub>2</sub>PN were prepared by the condensation of commercially available aniline, 3-nitroaniline and 3,5-dinitroaniline, respectively, with nadic anhydride (NA) in hot acetic acid followed by chemical imidization with acetic anhydride. The precipitated phenylnadimides were isolated by suction filtration from the cooled solution to yield white solids, mp 143 to 144 °C, 176 to 177 °C and 170 to 171 °C, respectively. The BZPN, mp 225 to 226 °C, and the NO<sub>2</sub>BZPN, mp 181 to 183 °C, were prepared similarly from the condensation of commercially available phthalic anhydride and 4-nitrophthalicanhydride, respectively, with the mononadimide derivative of MDA, mp 189 to 190.5 °C.

### PMR Solutions and Molding Powders

PMR-15 resin solutions were prepared at 50 wt % in methanol from 2.087 moles of BTDE, 3.087 moles of MDA, 2 moles of NE and 2 times the desired molar % of phenylnadimide or nitrophenylnadimide additive. BTDE solution (50 wt %) was prepared by heating, at the reflux temperature, a suspension of BTDA in methanol. After the BTDA dissolved, the solution was heated for an additional 2 hr.

PMR solutions were prepared at room temperature by adding NE, MDA and nitro-phenyl nadimide or phenyl nadimide additives all at once to the BTDE solution, and then adding an equivalent weight of methanol to maintain 50 wt % solids. Gentle heating and additional methanol were, in some cases, required to dissolve larger amounts of the NO<sub>2</sub>PN, DINO<sub>2</sub>PN and NO<sub>2</sub>BZPN additives. The amounts and types of additives investigated (expressed as a molar % of NE endgroups) in this study were 0, 1, 3, 5, 10, and 15 mole % PN; 5, 10, and 15 mole % NO<sub>2</sub>PN; 15 and 25 mole % DINO<sub>2</sub>PN; 5, 10, and 15 mole % BZPN; 5, 10, and 15 mole % NO<sub>2</sub>BZPN; and 15 and 30 mole % DINO<sub>2</sub>TOL. Molding powders were prepared by gently heating and stirring a portion of each PMR solution until the resin attained a syrup-like viscosity. The resin-syrup was then staged for 1 hr at 204 °C in a circulating air oven. The resultant foamy solid was ground in a mortar and pestle to provide a molding powder for neat resin disc preparation. The remainder of the PMR solutions were used for composite preparation as described in Section 2.4.

#### Neat Resin Discs and Weight Losses

Neat resin discs were prepared from approximately 1 g samples of each molding powder listed in Section 2.2 by curing in a 2.26 cm diameter matched metal die at 274 °C (NO<sub>2</sub>PN, DINO<sub>2</sub>TOL additives) or 316 °C (all others) for 2 hr. A pressure of 3.45 to 13.80 MPa was applied at 232 °C depending on the flow characteristics of the molten resin. The resultant resin discs were cut on a wafering dicing machine to provide four 0.63 by 0.63 cm by fabricated thickness (generally 0.13 to 0.23 cm) resin pieces of measurable surface area from the center of each resin disc and six small edge pieces. The four 0.63 cm<sup>2</sup> resin pieces were postcured at 316 °C for 17 hr and then were used for the thermo-oxidative screening study. All the resin samples were aged simultaneously in a single 316 °C circulating air oven having an air change rate of 100 cm<sup>3</sup>/min. Weight losses and dimensional changes were determined periodically during 1500 hr of exposure. The small edge pieces from the cut resin discs were used to determine glass transition temperatures (T<sub>g</sub>) at a heating rate of 20 °C/min on a Thermomechanical Analyzer (TMA) before and after the 316 °C air postcure treatment.

#### Composite Fabrication

Prepreg tape was made by drum winding unsized Celion 6000 graphite fiber (lot # HTA-7-2531) at 4.72 turns/cm and impregnating with the PMR solutions containing 0, 1, 3, and 5 mole % PN; 5, 10, and 15 mole % BZPN; and 5, 10, and 15 mole % NO<sub>2</sub>PN. This yielded prepreg containing 40 to 41 wt % monomers (calculated to provide cured laminates having 63 wt % fiber). Prepreg was dried on the rotating drum in ambient air for 3 to 6 hr and then allowed to stand overnight. Prepreg tapes were removed from the drum, cut into 7.6 by 20.3 cm plies, and stacked unidirectionally 12 plies thick. The prepreg stack was placed in a preforming mold and staged at 204 °C for 1 hr under a pressure of approximately 0.5 KPa. Composites were molded by placing staged prepreg into a matched metal die at room temperature. The die was inserted into a 316 °C press and, when the die thermo-couple indicated 232 °C, a pressure of 10.35 MPa (NO<sub>2</sub>PN, 274 °C cure), 6.70 MPa (NO<sub>2</sub>PN, 316 °C cure) or 3.45 MPa (all other formulations) was applied. After the mold reached the specified cure temperature, both temperature and pressure were maintained for 2 hr. The

mold was then allowed to cool to at least 177 °C before releasing the pressure and disassembling. The weights of all the laminates plus flash were up to 0.2 g less than the staged prepreg. Weight of flash divided by the weight of composite plus flash was called the resin flow and never exceeded 0.7 percent.

This amount of resin flow was deemed minimal. The laminates were cut into nine 2.54 by 6.67 cm coupons. Seven coupons from each laminate were postcured in air from ambient to 316 °C over 2 hr, held at 316 °C for 16 hr and then slowly cooled to room temperature. Postcure weight losses were between 0.34 and 1.44 percent, but generally ranged from 0.6 to 0.9 percent. All the laminates were visually inspected for surface defects or cracks. Photomicrographs of the composite cross sections were examined to assure that the composites were void-free and had a uniform resin/fiber distribution.

### Composite Testing

Two unpostcured and two postcured coupons from each laminate were used to prepare flexural and interlaminar shear strength (ILSS) test specimens. Tests were run at ambient, 274, and 316 °C. Flexural strength tests were performed in accordance with ASTM Test for Flexural Properties of Plastics and Electrical Insulating Materials (D790-71). A three point load fixture with fixed space of 5.1 cm was used. Specimens ranged from 0.21 to 0.23 cm in thickness for all the laminates resulting in span to depth ratios of 24.7 to 21.7, respectively. ILSS tests were performed essentially in accordance with ASTM Tests for Apparent Interlaminar Shear Strength of Parallel Fiber Composites by Short Beam Method (D2344-76) using a constant span to depth ratio of five. The rate of center loading for flexural and ILSS tests was 0.13 cm/min. Flexural and ILSS tests were conducted in an environmental heating chamber following a 15 min equilibration at test temperature. The mechanical property values reported are averages of three flexural strength tests and three or four ILSS tests at each condition. Fiber content was determined for all laminates before aging by the use of a  $H_2SO_4/H_2O_2$  digestion procedure. Flexural data were not normalized to a common fiber volume percent because the narrow range of fiber weight percent (average =  $64.1 \pm 1.4$ ) found by digestion causes an insignificant effect on the normalization of the raw flexural data (as shown later). The remaining five 2.54 by 6.67 cm test coupons from each laminate were used for 2400 hr isothermal exposure. All coupons including the control were aged simultaneously in a single 316 °C circulating air oven having an air change rate of 100  $cm^3/min$ . Composite weight loss measurements were made throughout the exposure period. Every 600 hr one coupon from each laminate was removed for 316 °C mechanical testing as described above until at 2400 hr only two coupons remained.

## RESULTS AND DISCUSSION

### Weight Loss Investigations

Neat Resin Weight Loss. - Resin weight loss was determined on a weight loss/surface area basis as described in Section 2.3. PMR-15 cured at 274 °C (designated LT PMR-15 for low temperature) and PMR-15 compositions containing up to 15 molar % additives of PN,  $NO_2PN$  or BZPN exhibit up to a 10 percent increase in weight loss after 1500 hr of exposure in air at 316 °C compared to PMR-15 cured at 316 °C (designated PMR-15 control). Resins incorporating 10 to 15 mole % of PN,  $NO_2PN$  or BZPN exhibit approximately the same weight loss after

1500 hr of 316 °C air exposure, presumably reflecting the similar aliphatic contents. However, the use of 15 and 25 mole % DINO<sub>2</sub>PN, 5 to 15 mole % NO<sub>2</sub>BZPN or 15 and 30 mole % DINO<sub>2</sub>TOL increases resin weight loss significantly greater than 10 percent. The increased weight loss was used to eliminate DINO<sub>2</sub>PN, NO<sub>2</sub>BZPN and DINO<sub>2</sub>TOL additives from the composite studies. The 10 and 15 molar % additions of PN to PMR-15 were also eliminated from the study due to the higher composite weight losses reported (ref. 9) for PMR compositions containing more than 8.1 mole % of PN. Thus, only 0 to 5 mole % PN and 5 to 15 mole % BZPN as control levels of additives and 5 to 15 mole % NO<sub>2</sub>PN as a low temperature curing initiator were investigated in the composite portion of the study.

Composite Weight Loss. - The weight loss of Celion 6000/PMR-15 composites with the additives is shown in figure 1 as a function of 316 °C air exposure time. The figure shows three regions of interest, labeled A to C as weight loss increases. The standard deviation of individual data points within the three regions was generally ±0.2 to 0.3 percent. The larger weight loss (lower line) of region A represents LT PMR-15, 5 mole % NO<sub>2</sub>PN cured at 316 °C, and all PN containing compositions. The middle of region A represents PMR-15 control and 5 mole % NO<sub>2</sub>PN cured at 274 °C. The smaller weight loss (upper line) of region A represents all BZPN containing compositions. The smaller weight losses of regions B and C represent 10 and 15 mole % NO<sub>2</sub>PN compositions cured at 274 °C, respectively, while the larger weight losses of regions B and C represent the same compositions cured at 316 °C. For practical purposes there is little difference in composite weight losses up to 1200 hr for all PMR-resins containing up to 10 mole % of any additives. However, with longer exposure times a clear distinction between the type and amount of additive is observed. There are two trends noted beyond 1200 hr. First, increasing amounts of NO<sub>2</sub>PN additive results in a corresponding increase in composite weight loss. Second, curing at 316 °C with NO<sub>2</sub>PN additives rather than curing at 274 °C, consistently results in increased weight loss. Curing at 274 °C with no additive reverses this trend. Thus, PMR-15 without low temperature curing additives should be cured at 316 °C, not 274 °C, to obtain minimum weight loss, or maximum thermo-oxidative stability, while PMR-15 with low temperature curing additives should be cured at the lower temperature, to obtain minimum weight loss.

Increased weight loss for higher concentrations of NO<sub>2</sub>PN additive may be rationalized on the basis that NO<sub>2</sub>PN continues to act as a site for increased free radical activity during long term 316 °C aging. Further increases in weight loss at the same level of NO<sub>2</sub>PN additives for samples cured at 316 °C, rather than 274 °C, can be rationalized if increased free radical activity during curing leads to an increased degradation rate during long term aging. The overall trend of the composite weight loss data is consistent with the neat resin weight loss data discussed in Section 3.1.1. The only major exception is for composites with 5 to 15 mole % BZPN. These composites exhibit slightly less weight loss than PMR-15. This difference could not be explained because of differences in resin synthesis, sample size, or aging conditions.

#### Property Investigations

Glass Transition Temperatures. - The glass transition (T<sub>g</sub>) temperatures of neat resin discs were determined by TMA analyses before and after postcure. Data for unpostcured specimens are shown in figure 2. It is apparent that a significant variation in T<sub>g</sub> arises from changes in cure temperatures and amount of additive. The PMR-15 control (0 mole % additive) cured at 316 °C exhibits a



Tg of 270 °C. Curing PMR-15 at 274 °C causes the Tg to decrease to 190 °C. In neither case does the Tg reach the cure temperature which implies that the resin vitrifies at an intermediate extent of reaction resulting in a low Tg.

The addition of 5 to 15 mole % PN or BZPN to PMR-15 causes a slight decrease in the Tg of samples cured at 316 °C. It is presumed that the decrease is due to plasticization of the resin by the monophenylnadimide reactants. This effect should be contributing for all the additives in this study. The addition of 5 to 15 mole % NO<sub>2</sub>PN to PMR-15 cured at 274 °C appears to increase the extent of reaction to somewhat offset the plasticization effect and raise the Tg to 216 °C. This increase may be due to increased rate of reaction or incorporation of the NO<sub>2</sub>PN into the network in new (and currently undefined) rereaction paths. The ability to enhance the extent of reaction at the lower cure temperature is the desirable aspect of the NO<sub>2</sub>PN additives.

Curing the resins with NO<sub>2</sub>PN at 316 °C causes changes which are not as consistent as the additive effects noted above. At 5 and 10 mole % additive, the Tg is lower than the Tg of resins containing the same levels of non-nitro additives. The plasticization effect should be comparable for all the additives, so it appears that some additional chemical effects are present. One such effect could be increased retardation or termination activity of the NO<sub>2</sub>PN additives in this temperature range. The 15 mole % NO<sub>2</sub>PN sample exhibits a unique Tg which does approach the 316 °C cure temperature. This may reflect a larger extent of reaction resulting from the greater level of additive and its activity at this higher temperature or that alternate reaction paths are occurring with NO<sub>2</sub>PN at higher cure temperatures.

After 316 °C postcure, all samples, except those with NO<sub>2</sub>PN additive cured at 316 °C, exhibited a Tg of 325±5 °C. This reflects the completion of cross-linking and initial thermo-oxidative crosslinking typical of PMR-15. Samples containing NO<sub>2</sub>PN cured at 316 °C did not exhibit as large an increase in Tg after the postcure. The Tg for samples containing 5 and 10 mole % NO<sub>2</sub>PN did not reach 325 °C. This again suggests that the activity of the NO<sub>2</sub>PN at the 316 °C cure temperatures may be competing with usual thermal and oxidative reactions in an undesirable way. This is also evident in the thermo-oxidative stability of these samples as reflected in retention of weight and mechanical properties (discussed in later sections).

Composite Fabrication. - The fabrication of mechanically sound laminates using thermosetting matrix resins requires appropriate balance of resin melt and flow for consolidation and resin cure rate which ultimately restricts flow and solidifies the material. Because melt/flow and cure rate are both thermally activated, an optimal time/temperature cure schedule must be sought to match the rheological and kinetic behavior of the matrix resin. By increasing the rate of cure using additives such as NO<sub>2</sub>PN, the time to vitrification or gelation at any temperature is decreased. This imposes a constraint on any low temperature cure since the cure reaction may initiate before complete melt or adequate flow of the resin is obtained. This can result in poorly consolidated composites. A second constraint on any low temperature cure is the extent of reaction achieved in the matrix resin during the chosen time/temperature cycle. Low levels of cure, as reflected by low Tg of the resin, usually correlate with low mechanical properties. The extent of cure must be advanced to provide resin strengths in the composite which are adequate to withstand the stresses resulting from subsequent postcure procedures.

Prior calorimetric studies (ref. 8) indicated that NO<sub>2</sub>PN additives can initiate a cure exotherm at temperatures as low as 232 °C. However, composites cured at temperatures below 274 °C were poorly consolidated or often blistered during postcure. These observations reflect the constraints noted above. It is likely that a more extensive screening of cure and postcure cycles to circumvent the blistering could reduce the useful cure temperature slightly below 274 °C. However, the cure pressure required at 274 °C (10.35 MPa), already reflects limited resin flow relative to the standard PMR-15 cure and implies that significant additional reduction in cure temperature would be unlikely.

Initial Composite Mechanical Properties. - Table II shows the initial composite mechanical properties (flexural strength and ILSS) at 274 and 316 °C versus the amount and type of additive to PMR-15 resin. All room temperature properties (not shown in Table II) ranged from 1490 to 1766 MPa for flexural strength and 99.4 to 113.2 MPa for ILSS. No discernable trend in the room temperature properties was observed with varying additive levels or low temperature curing of PMR-15. This is presumably because the testing is done far below the T<sub>g</sub>'s of all the resins. However, at elevated test temperatures, a significant decrease in mechanical properties is observed with increasing additive levels. At all levels of non-nitro additives the unpostcured 274 or 316 °C properties are significantly lower than those of the PMR-15 control. After postcure, composites with 1 to 5 mole % PN exhibit 274 °C properties that are similar to the control and 316 °C properties that are slightly lower than those of the control. However, composites having 5 to 15 mole % BZPN exhibit 316 °C properties which remain significantly lower than those of the control. This is presumably due to the slightly lower T<sub>g</sub> (310 to 317 °C versus 325 °C) of the BZPN compositions. Thus, the use of any level of phenylnadimide additive in PMR-15 causes an observable decrease in initial elevated temperature properties.

Elevated temperature mechanical properties for composites using NO<sub>2</sub>PN as a cure accelerator are shown in Table III. At both 274 and 316 °C, a significant decrease in mechanical properties of the unpostcured composites, compared to PMR-15 control, is again observed with increasing additive levels. Addition of 5 to 15 mole % NO<sub>2</sub>PN or curing at 316 °C does increase elevated temperature, unpostcured properties compared to LT PMR-15, however, the properties remain significantly below those of the PMR-15 control. This is presumably due to the significantly lower T<sub>g</sub>'s (fig. 2). After postcure, composites with 5 to 15 mole % NO<sub>2</sub>PN exhibit no discernable differences in elevated temperature mechanical properties whether curing was done at 274 or 316 °C. The properties determined at 274 °C are very close to those of PMR-15 control, however, a significant decrease in the 316 °C properties is observed. Thus, the use of any level of PN, BZPN, or NO<sub>2</sub>PN additive will cause an observable decrease in initial elevated temperature properties. In addition, even with no additive, the low temperature curing of PMR-15 does not produce composites with 316 °C mechanical properties comparable to PMR-15 cured at 316 °C.

Long Term Composite Mechanical Properties. - Figures 3 and 4 show the 316 °C composite mechanical properties (ILSS and flexural strength) of PMR-15 with various additives as a function of 316 °C air exposure time. The flexural data have not been normalized to a common fiber volume percent. Composite digestion analyses showed that the fiber weight percent ranged from 62.2 to 66.7 percent with an average of 64.1±1.4 percent for the 15 composites in this study. This deviation is minimal and results in such a small range of fiber volumes that normalization would have little effect on the general trends of the flexural data. The standard deviation of an individual data point after

600 to 2400 hr exposure was, for ILSS, almost always less than  $\pm 2.7$  MPa and, for flexural strength, generally  $\pm 27$  to 41 MPa. The postcured (0 hr) data points and standard deviations of the two mechanical properties for all 15 composites are given in the last column of Table II and III. The standard deviation in many 0 hr cases is considerably greater than described above for aged samples.

The overall trends in the mechanical properties of the composites fabricated with 5 mole % additive levels compared to PMR-15 control are evident in figures 3 and 4. PMR-15 composites formulated with 5 mole % PN or BZPN show a slight decrease in initial 316 °C properties (as discussed in Section 3.2.3). The properties increase during 1200 hr of 316 °C aging until composites with 5 mole % PN show properties nearly identical to the PMR-15 control. Thus, the plasticizing effect of small amounts of phenylnadimide additive, as reflected by decreased initial properties, disappears with prolonged oxidative aging. This trend has been previously reported (ref. 9). Properties for composites using low temperature cured PMR-15 coincide with the lower limit of region B in both figures. The composites formulated with 10 to 15 mole % BZPN (not shown in figs. 3 and 4) exhibit a further decrease in initial properties as previously discussed in Section 3.2.3. These properties also increase during 1200 hr of 316 °C aging until they are almost equivalent to the lower limit of 5 mole % non-nitro additives. Thus, the relatively low initial mechanical properties due to low temperature (274 °C) incomplete curing of PMR-15 and/or the plasticizing effect of 10 to 15 mole % BZPN disappear during oxidative aging as was observed with 5 mole % levels of PN or BZPN additive.

The use of 5, 10, and 15 mole %  $\text{NO}_2\text{PN}$  additive levels also results in a significant decrease of initial mechanical properties. The trend in properties of composites fabricated with 5 mole %  $\text{NO}_2\text{PN}$  levels are shown in figures 3 and 4 as region C. They exhibit an increase during 1200 hr of 316 °C aging to equal the property levels of 5 mole % non-nitro additives (region B). Thus the plasticizing effect again tends to disappear during oxidative aging. Composites having 10 to 15 mole %  $\text{NO}_2\text{PN}$  additive levels exhibit a similar trend, but a greater decrease in long term mechanical properties. This decrease presumably corresponds to the greater rate of weight loss, or degradation, of these composites (fig. 1). Beyond 1200 hr, the properties of the 5 mole %  $\text{NO}_2\text{PN}$  formulation cured at 274 °C are represented by the upper limit in region C. When cured at 316 °C, this formulation exhibits properties on the lower limit of region C. Thus, the trend in mechanical property retention closely correlates with the trend in increased 316 °C weight loss. It may then be concluded that 274 °C cure of  $\text{NO}_2\text{PN}$  formulations promotes significant resin degradation as reflected in both weight and property retention beyond 1200 hr of 316 °C exposure. This effect is accentuated by 316 °C curing.

## CONCLUSIONS

Based on the results of this investigation the following may be concluded:

1. Graphite fiber/PMR-15 composites can be cured at temperatures as low as 274 °C by using a nitrophenylnadimide cure accelerator.
2. PMR-15 composites cured with phenylnadimide additive (with or without nitro substituents) exhibit decreased initial mechanical properties compared to standard PMR-15.

3. PMR-15 composites cured with nitrophenylnadimides at 274 °C exhibit increased levels of weight loss and a corresponding loss of mechanical properties during 316 °C exposure compared to standard PMR-15. PMR-15 composites cured with nitrophenylnadimides at 316 °C exhibit additional weight loss and increased loss of mechanical properties.

4. PMR-15 composites cured at 274 °C with no additive exhibit slightly less thermo-oxidative stability, lower initial properties, and more rapid loss of mechanical properties when compared to PMR-15 composites cured at 316 °C.

#### BIOGRAPHY

Dr. William B. Alston is presently a Materials Research Engineer with the Propulsion Laboratory of the U.S. Army Aviation System Command, assigned to the Polymer Matrix Composites Section of the NASA Lewis Research Center since 1971. He received his B.S. in Chemistry from the University of Wisconsin, M.S. and Ph.D. in Chemistry from the University of Iowa. His current research is in the high temperature polymer composite areas of monomer and polymer synthesis, crosslinking methods and matrix resin characterization.

Dr. Richard W. Lauver has been employed at NASA Lewis since 1974. He received a B.A. in Chemistry from Knox College and a Ph.D. in Chemistry from the University of Illinois. His current research is in the area of chemical characterization of polymer and composite materials.

#### REFERENCES

1. T.T. Serafini, P. Delvigs, and G.R. Lightsey, "Thermally Stable Polyimides from Solutions of Monomeric Reactants," *J. Appl. Polym. Sci.* **16** (4) 905-915 (1972).
2. P. Delvigs, T.T. Serafini, and G.R. Lightsey, "Addition-Type Polyimides from Solutions of Monomeric Reactants," *Materials Review for '72*, Society of Aerospace Materials and Process Engineers, Azusa, CA, 1972, pp. III-B-Seven-1 to III-B-Seven-15.
3. T.T. Serafini, P. Delvigs, and W.B. Alston, "PMR Polyimides-Review and Update," *National SAMPE Symposium and Exposition, Proceedings*, Society for the Advancement of Material and Process Engineering, Azusa, CA, 1982, pp. 320-335.
4. T.T. Serafini, P. Delvigs, and R.D. Vannucci, "Lower-Curing-Temperature PMR Polyimides," 36th Annual SPI Conference of the Reinforced Plastics/Composites Institute, 16-20 February 1981.
5. P. Delvigs, "Lower-Curing-Temperature PMR Polyimides," *Polym. Compos.*, **4**, (3) 150-153 (1983).
6. P. Delvigs, "PMR Polyimides from Solutions Containing Mixed End-Caps," *Proceedings of High Temperature Polymer Matrix Composites Conference*, NASA-Lewis Research Center, Cleveland, Ohio, March 16-18, 1983. NASA CP in progress.

7. C.N. Sukenik, V. Malhotra, and U. Varde, "Inter- and Intra-Molecular Reactions of Substituted Norbornenyl Imides," Polym. Prepr., 25 (1) 104-105 (1984).
8. R.W. Lauver, "Chemical Control of Rate and Onset Temperature of Nadimide Polymerization," Proceedings of High Temperature Polymer Matrix Composites Conference, NASA-Lewis Research Center, Cleveland, Ohio, March 16-18, 1983 NASA CP in progress. (And, "Chemical Approach for Controlling Nadimide Cure Temperature and Rate," U.S. Patent No. 4,455,418 (1984).
9. R. H. Pater, "Novel Improved PMR Polyimides," SAMPE J., 17 (6) 17-25 (1981).

TABLE I. - MONOMERS AND ADDITIVES USED IN POLYIMIDE SYNTHESIS

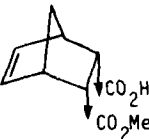
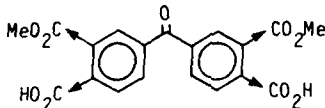
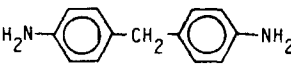
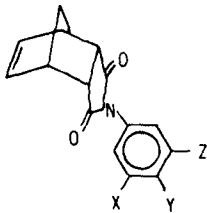
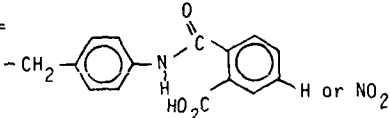
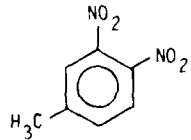
Structure	Name	Abbreviation
	Monomethyl Ester of Endo-5-Norbornene-2,3-Dicarboxylic Acid	NE
	Dimethyl Ester of 3,3',4,4'-Benzophenonetetracarboxylic Diacid	BTDE
	4,4'-Methylenedianiline	MDA
	X=Y=Z=H Endo-N-Phenylnadimide X=NO <sub>2</sub> , Y=Z=H Endo-3-Nitrophenylnadimide X=Z=NO <sub>2</sub> , Y=H Endo-3,5-Dinitrophenylnadimide X=Z=H, Y=	PN NO <sub>2</sub> PN DINO <sub>2</sub> PN
		
	H=Phthalamide-acid of Mononadimide of MDA (Benzylic containing PN)	BZPN
	NO <sub>2</sub> =4-Nitrophthalamide-acid of Mononadimide of MDA (Nitro group in Benzylic containing PN)	NO <sub>2</sub> BZPN
	3,4-Dinitrotoluene	DINO <sub>2</sub> TOL

TABLE II. - INITIAL ELEVATED-TEMPERATURE MECHANICAL PROPERTIES  
OF COMPOSITES OF CELION 6000 GRAPHITE FIBER/PMR-15 PLUS  
NON-NITRO ADDITIVES

Type of additive to PMR-15	Amount, mole %	Unpostcured		Postcured	
		Test temperature, °C			
		274	316	274	316
Flexural strength, MPa					
None <sup>b</sup>	-----	970±29	612±36	972±26	906±31
PN	1	788±34	348±8	866±22	722±43
PN	3	839±57	455±91	935±42	735±43
PN	5	774±3	343±53	961±53	764±38
BZPN	5	(a)	266±33	(a)	650±44
BZPN	10	(a)	369±58	(a)	357±52
BZPN	15	(a)	356±92	(a)	436±166
Interlaminar shear strength, MPa					
None <sup>b</sup>	-----	45±3	35±4	58±2	49±1
PN	1	43±1	33±1	52±2	45±1
PN	3	43±1	34±2	53±1	45±1
PN	5	43±1	35±4	54±2	45±2
BZPN	5	(a)	35±1	(a)	39±4
BZPN	10	(a)	31±2	(a)	38±3
BZPN	15	(a)	35±6	(a)	39±3

<sup>a</sup>Not determined.

<sup>b</sup>PMR-15 control.

TABLE III. - INITIAL ELEVATED-TEMPERATURE MECHANICAL  
PROPERTIES OF COMPOSITES OF CELION 6000 GRAPHITE  
FIBER/PMR-15 PLUS NITRO ADDITIVES

Amount of NO <sub>2</sub> PN additive, mole %	Cure temper- ature, °C	Unpostcured		Postcured	
		Test temperature, °C			
		274	316	274	316
Flexural strength, MPa					
0 <sup>c</sup>	316	970±29	612±36	972±26	906±31
0 <sup>d</sup>	274	165±12	103±1	892±47	600±25
5	↓	213±9	96±25	826±18	382±45
10	↓	335±56	187±63	822±76	428±54
15	↓	439±29	299±74	820±25	371±54
5	316	651±73	439±49	802±70	496±56
10	316	614±36	362±23	832±7	440±86
15	316	706±47	504±50	912±56	397±40
Interlaminar shear strength, MPa					
0 <sup>c</sup>	316	45±3	35±4	58±2	49±1
0 <sup>d</sup>	274	(a)	(b)	49±1	39±2
5	↓	(a)	(b)	50±1	39±5
10	↓	(a)	(b)	48±4	35±2
15	↓	(a)	(b)	49±2	35±3
5	316	43±3	35±4	50±3	39±2
10	316	44±4	35±4	46±2	40±5
15	316	41±3	40±1	51±1	38±4

<sup>a</sup>Thermoplastic.  
<sup>b</sup>Not determined.  
<sup>c</sup>PMR-15 control.  
<sup>d</sup>LT-PMR-15



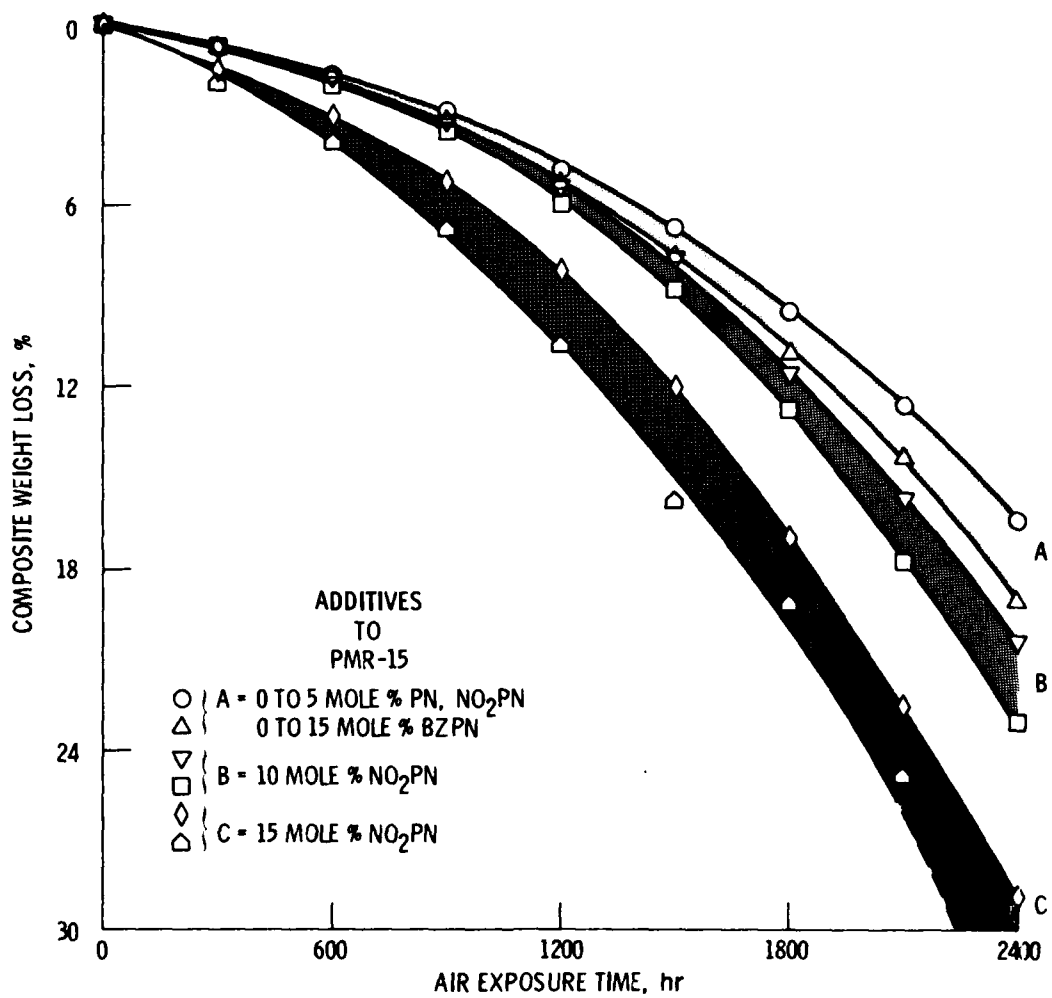


Figure 1. - Trends in 316° C composite weight loss as a function of additives to PMR-15.

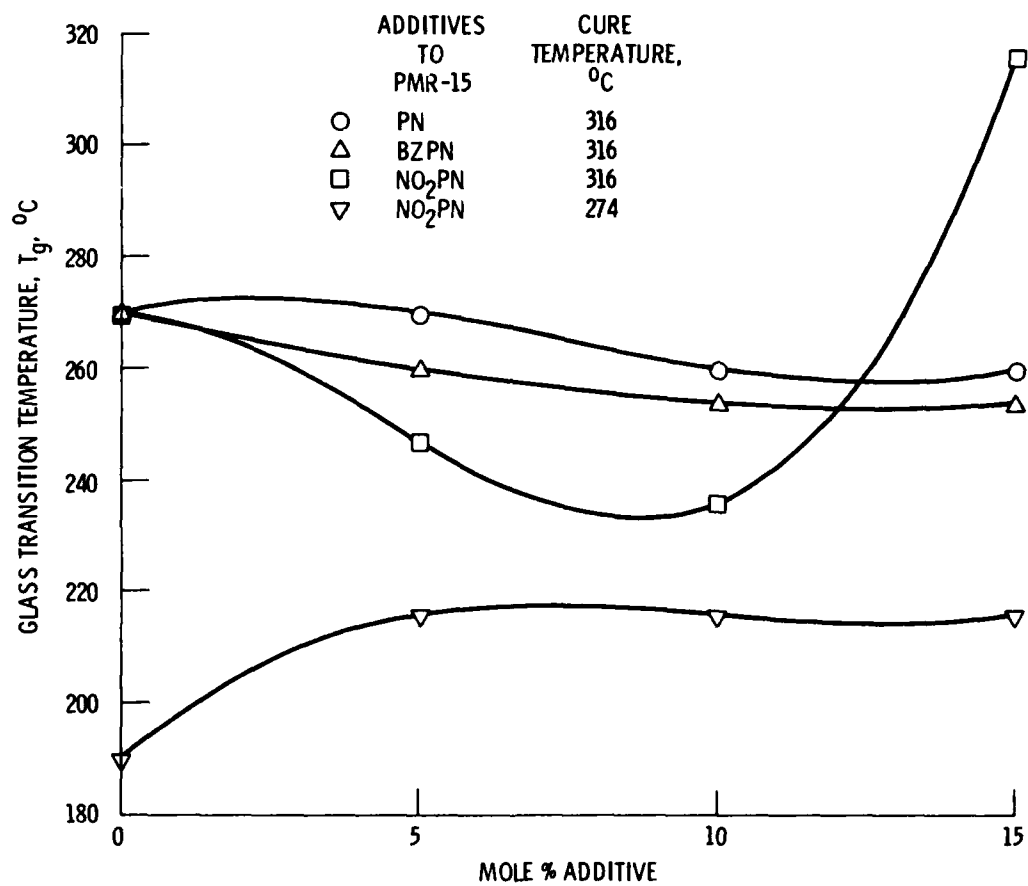


Figure 2. - Trends in glass transition temperature as a function of additives to PMR-15.

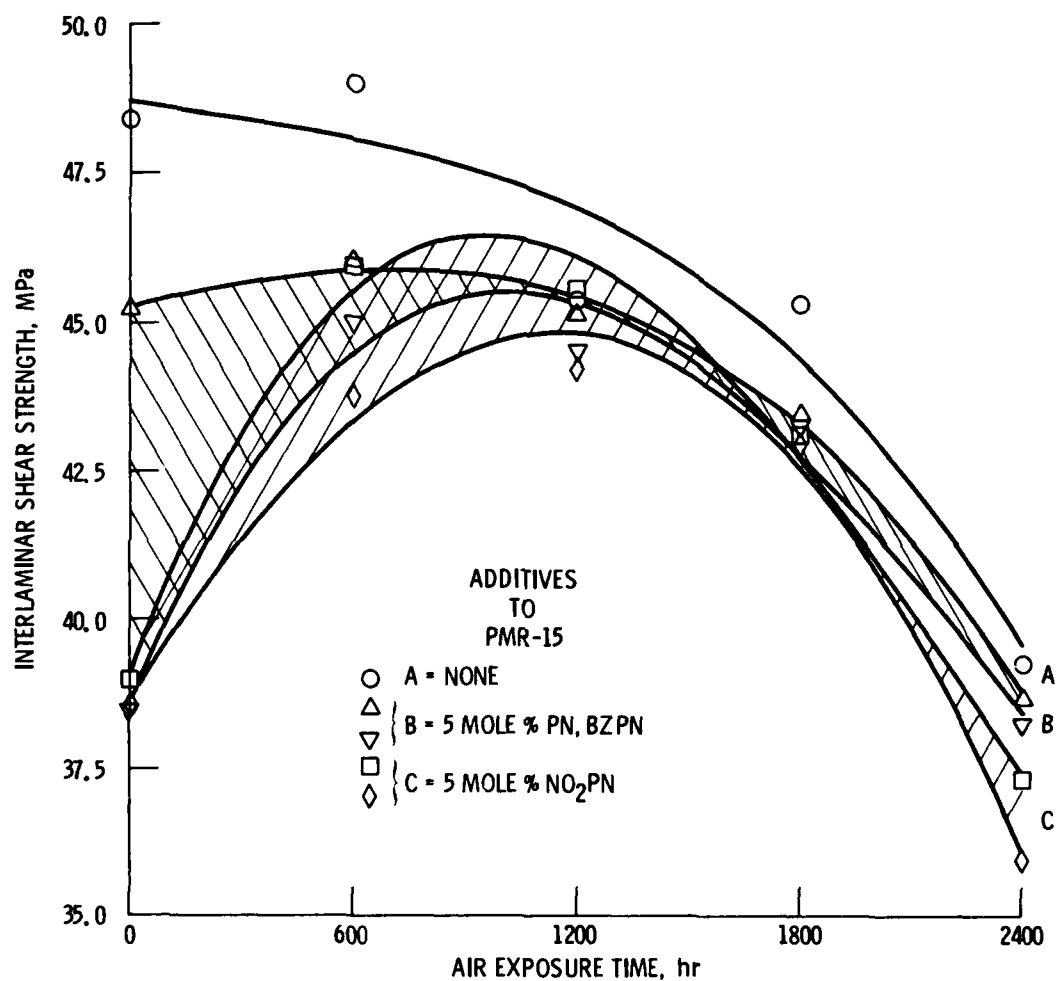


Figure 3. - Trends in retention of 316° C interlaminar shear strength as a function of additives to PMR-15.

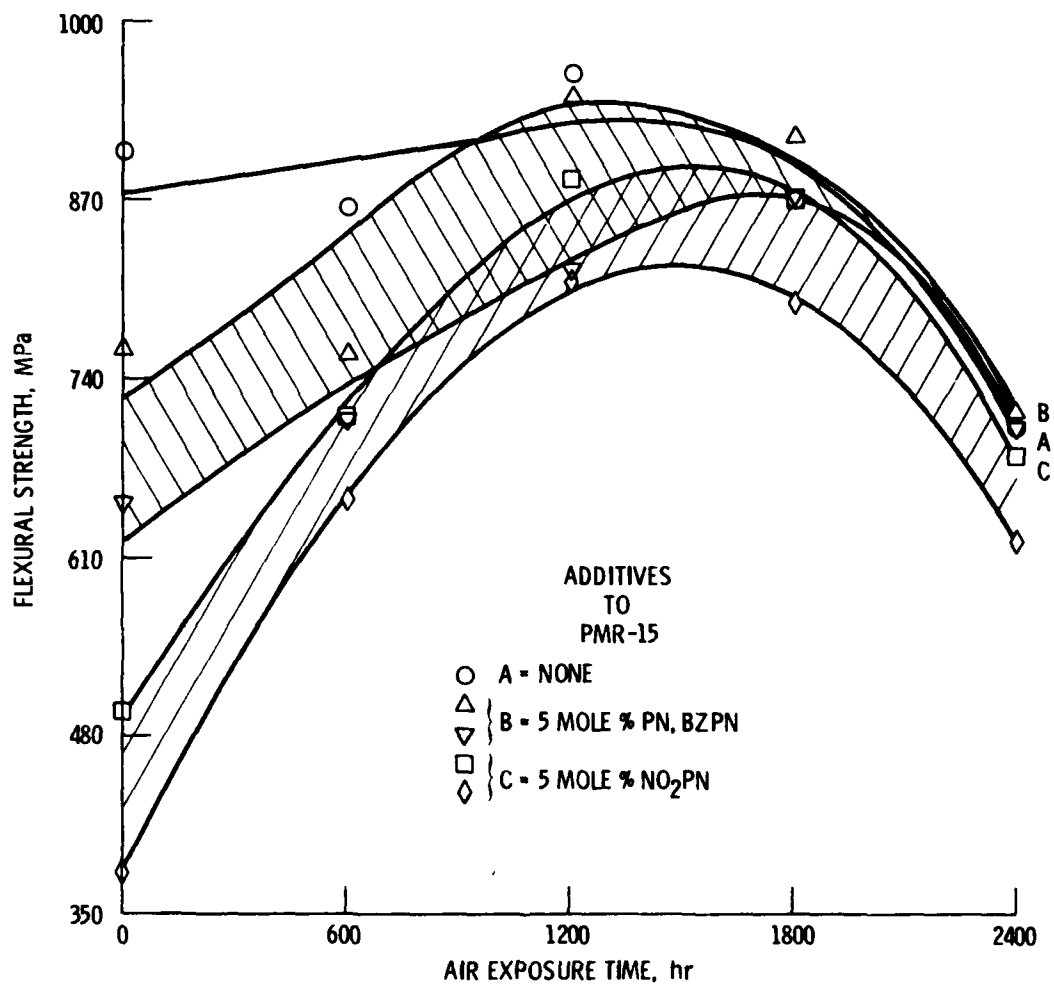


Figure 4. - Trends in retention of 316°C flexural strength as a function of additives to PMR-15.

1. Report No. NASA TM-86902 USAAVSCOM-TR-84-C-20		2. Government Accession No. <b>AD-A150529</b>		3. Recipient's Catalog No.	
4. Title and Subtitle Effect of Substituted Phenylnadimides on Processing and Properties of PMR Polyimide Composites				5. Report Date	
				6. Performing Organization Code 505-33-32	
7. Author(s) William B. Alston and Richard W. Lauver				8. Performing Organization Report No. E-2380	
				10. Work Unit No.	
9. Performing Organization Name and Address NASA Lewis Research Center and Propulsion Laboratory U.S. Army Research and Technology Laboratories (AVSCOM) Cleveland, Ohio 44135				11. Contract or Grant No.	
				13. Type of Report and Period Covered Technical Memorandum	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546 and U.S. Army Aviation Systems Command, St. Louis, Mo. 63120				14. Sponsoring Agency Code	
15. Supplementary Notes William B. Alston, Propulsion Laboratory, AVSCOM Research and Technology Laboratories, Lewis Research Center, Cleveland, Ohio 44135; Richard W. Lauver, NASA Lewis Research Center. Prepared for the Thirtieth National SAMPE Symposium and Exhibition, Anaheim, California, March 19-21, 1985.					
16. Abstract Three nitrophenylnadimide cure initiators and two phenylnadimides (without nitros) were evaluated as additives to PMR-15 resins and Celion 6000 graphite fiber composites. The results of a resin screening study eliminated all of the additives except 3-nitrophenylnadimide (NO <sub>2</sub> PN) for use as a low temperature curing additive for PMR-15. Thus, NO <sub>2</sub> PN and the two control additives were investigated in PMR-15 formulations from which Celion 6000 graphite fiber/PMR-15 composites were processed both with low temperature (274 °C) and normal (316 °C) cure cycles. Comparisons of the two processing cycles, the resultant glass transition temperatures (T <sub>g</sub> ), the ambient, 274 and 316 °C composite mechanical properties determined before and after 316 °C postcure, the 316 °C thermo-oxidative weight losses and the retention of 316 °C composite mechanical properties are presented. Empirical correlations of the type and amount of nadimide additives with processing parameters, T <sub>g</sub> , composite mechanical properties, composite thermo-oxidative stability and long term retention of 316 °C composite mechanical properties are also presented. It was shown that PMR-15 composites could be fabricated using a low temperature (274 °C) cure with nitrophenylnadimide additives. However, the use of any type of phenylnadimide additives (nitro or non-nitro) or the lower temperature curing of PMR-15 without additives resulted in composites that exhibited a combination of decreased initial mechanical properties, lower retention of elevated temperature mechanical properties and/or increased composite weight loss compared to conventionally cured PMR-15 composites.					
17. Key Words (Suggested by Author(s)) PMR; Polyimides; Graphite fiber; Composites; Thermo-oxidative stability; Thermomechanical			18. Distribution Statement Unclassified - unlimited STAR Category		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of pages	
				22. Price*	

**END**

**FILMED**

**3-85**

**DTIC**

